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Characterization of tar generated from the mixture of municipal solid waste and coal pyrolysis at 800 °C

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Abstract

Nowadays, comprehensive perception of the tar characteristics generated from municipal solid waste (MSW) and coal to guide pyrolysis or gasification gas yield upgrading and cleaning has attracted massive research attention. In this study, MSW and coal samples were chosen as principal components. The mixture of these products was pyrolyzed in a horizontal tube furnace at 800 °C with a heating rate of 20 °C/min. The tar derived from the pyrolysis of this mixture was further studied. Gas chromatography–mass spectrometry (GC–MS) coupled with a trace GC and a nuclear magnetic resonance (NMR) spectrometer was applied to investigate the tar composition and characterization along with their molecular chemical structures. ^{1}H and ^{13}C NMR spectra indicated that the functional groups of the tar derived from the mixture of MSW and coal were dominant at the resonances of 0.9–1.8 ppm, 1.5–2.6 ppm and 3.8–4.1 ppm for ^{1}H, 10–40 ppm and 60–80 ppm for ^{13}C. The results from GC–MS showed that the tar derived from the mixture of MSW and coal contained about 20 major chemical compounds such as benzene, methyl isobutyl, toluene, xylene, phenol, cresol, naphthalene and others.

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Keywords: MSW; Coal; Pyrolysis; Tar; NMR; GC–MS

1. Introduction

It is known that the depletion of fossil fuels has become a major topic which continuously raises the human issues associated with its negative environmental consequences. A robust combination of fossil fuels (e.g., coal)

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with alternative sources of energy such as biomass, could delay the depletion trend. Municipal solid waste (MSW) is considered as one of the major biomass sources that can be converted into value-added gaseous or liquid products via promising thermochemical technologies [1,2]. However, due to the diversity of feedstock, synthetic gas from pyrolysis or gasification contains high levels of various impurities. The liquid tar is one of the dominating impurities which can lead to significant operational problems in downstream reactors by blocking outlet channels, filters and gas coolers [3]. Recently, numerous mechanisms and technologies (e.g., catalytic tar cracking, thermal tar cracking, etc.) have been developing for a certain level of tar reduction. Nevertheless, despite such enormous efforts, ultimate tar removal is still a challenging issue during gasification and pyrolysis. As a result, insufficient studies have been carried out to comprehensively characterize tar composition with respect to the mixture of MSW and coal components. Hence, an advanced analysis of the chemical functions involved in this mechanism is needed in order to perceive the tar composition. In addition, it is well known that tar has numerous heavy components and it is also considered as a complex compound. Fourier Transforms Infrared (FTIR) spectroscopy and gas chromatography–mass spectrometry (GC–MS) have been broadly used to identify the tar composition. In comparison with FTIR or GC, the NMR methods are considered as nondestructive and have been applied in numerous research investigations for the analysis of biomass polymers, cellulose, char or coal [4–10]. However, only a few studies have applied NMR as a supplementary research tool for tar characterization, despite the applicability and usefulness of NMR testing to quantify and identify structural features in complex mixtures beyond the measurement range of traditional GC. According to Diaz and Blanco [11] and Morgan et al. [12], NMR can identify molecular chemical structures and their connections with other molecules following the chemical shift values. In this paper, the characteristics of tar samples derived from the pyrolysis of mixed samples (MSW and coal) with a mass ratio of 1:1 were studied. The main compositions and corresponding molecular bonds of tar were identified by GC–MS and a JNM-ECA 500 Series FT Nuclear Magnetic Resonance Spectrometer. A wide-scale understanding of tar composition will benefit the comprehensive characterization of tar and provide essential information for tar removal processes.

2. Materials and methods

2.1. Materials and sampling

A standard ASTM D 5231-92 (2003) procedure was applied for collection of representative MSW samples. The sorting process was carried out in two stages, imitating the process of a typical mechanical sorting plant. After separation of recyclables in the first stage, the second stage was carried out to sort the combustible and non-combustible fractions. Thus, two samples were retrieved, a combustible fraction (mixed paper, mixed plastic, wood, textile and leather), and organics (food waste, green waste) from the second stage of sorting. The combustible fraction was shredded and sieved into particles of approximately 1 mm in size and mixed before performing the experiments to ensure representative MSW samples from the different materials. Coal samples (derived from the Shubarkol pit mines of Central Kazakhstan region) were retrieved by mixing and quartering. Then the samples were crushed and sieved to a size of 1600 μm. Proximate and ultimate analyses of samples are given in Table 1. Calorific values were determined using a bomb calorimeter.

Table 1. Proximate and ultimate analyses (wt %) of the model components.

MSW				Coal (Shubarkol)			
Proximate		Ultimate		Proximate		Ultimate	
Composition	Weight (%)	Composition	Weight (%)	Composition	Weight (%)	Composition	Weight (%)
Moisture	4.4	C	46.16	Moisture	5.96	C	69.72
Volatiles	65.2	H	6.23	Volatiles	40.3	H	6.05
Fixed carbon	3.5	N	4.18	Fixed carbon	51.3	N	1.71
Ash	21.59	S	0.26	Ash	2.44	S	1.05
GCV[a] (MJ/kg)	17.77	O	43.17	GCV[a] (MJ/kg)	26.97	O	21.47

[a]Gross calorific value (GCV).

2.2. Pyrolysis testing

The pyrolysis experiments carried out in a horizontal quartz tube reactor were described in detail by Tokmurzin et al. [13] and a schematic diagram is highlighted in Fig. 1. The reactor was heated in an electrically-heated furnace. The inner diameter of the quartz tube is 54 mm and its length is 1000 mm. The furnace is supplied with nitrogen from a gas cylinder. The amount of supplied gas is measured using a flow meter. The sample was fixed in a ceramic tube, located in the middle of the quartz tube. Nitrogen with a purity of 99.5% was introduced at a flow rate of 2 L/min to maintain a residence time of 5–6 s in heated zone. About 20 g of sample was used for each test. The heated exit gas from the furnace was passed through series of 6 impingers with volume of 250 mL. The tar samples were dissolved in the isopropanol solution (99.7%) and these dissolved tar samples were extracted using a rotary evaporator. Each test was performed at least 2–3 times to assure measurement accuracy.

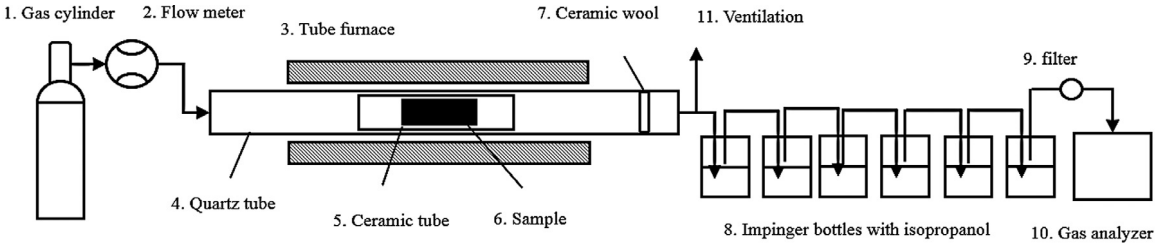


Fig. 1. Schematic diagram of the horizontal quartz tube experimental reactor.

2.3. Tar characterization

In this study, tar composition was detected using a GC–MS analyzer (TSQ 8000 EVO triple quadruple GC–MS/MS) coupled with a Thermo Scientific™ TRACE™ GC. Sample introduction was performed with a Thermo Scientific™ TriPlus™ RSH auto sampler. Chromatographic separation was implemented using a Thermo Scientific™ TraceGOLD™ TG-5SilMS film capillary column (60 mm length, 0.25 mm ID, and 0.25 μm film thickness). The transfer line and injector inlet temperature were set at 280 and 260 °C, respectively. The GC oven temperature was held at 100 °C for 2 min, increased to 280 °C at a rate of 10 °C/min, and then held constant at 280 °C for 15 min. The sample for NMR testing was prepared according to Derome [14] and Melkior et al. [7]. In the mass spectrometer, the injector was maintained at 260 °C. The volume of each injection was 0.2–0.5 μL. Helium (He) carrier gas was kept constant at 1.2 mL/min. The spectra of ^{1}H NMR (500 MHz) and ^{13}C NMR (500 MHz) were obtained using a JNM-ECA 500 Series FT NMR Spectrometer equipped with a two-channel 5 mm Royal Broad Band probe: HF Channel: 1H, 19F; LF Channel: all nuclei within 31P–15N. Deuterated chloroform ($CDCl_3$) was used as the solvent for tar derived from the mixture of MSW and coal to ameliorate the solubility of heavy tar components. Prior to the NMR analysis, the sample volume was set as 700 μL.

3. Results and discussion

3.1. Tar composition from NMR

Fig. 2 highlights the ^{1}H NMR spectra for tar samples produced at 800 °C. The types of H bonds depict a variety of H-alkane, H-allylic, H-alkyne, H-benzylic, H-amine, H-alcohol or ether, H-alkyl bromide, H-alkyl chloride, H-vinylic, H-aryl, and H-aldehyde, among which H-alkyl, H-allylic, H-alkyne, H-alkyl chloride and H-alkyl bromide are the major components. Fig. 2 shows the C bonds for the same tar samples. The peaks in the spectra indicate the possible existence of C-alkyl, RCH_3; C-alkyl, RCH_2R; C-alkyl, $RCHR_2$; C-alkyl halide or amine; C-alcohol or ether, C-alkyne, C-aryl or alkene, C-nitriles, C-amide carbonyl and C-carboxylic acids. The greater proportion of peaks (resonances) during 10–40 and 60–80 ppm indicates the generation of much more C-alkyl, RCH_3; C-alkyl, RCH_2R; C-alkyl, $RCHR_2$; C-alkyl halide or amine; C-alcohol or ether and C-alkyne. From the results above, it can be inferred that MSW plays a substantial part in influencing the composition and proportion of H and C bonds in the pyrolyzed tar. In addition, results show that advanced NMR spectroscopic techniques applied in this study

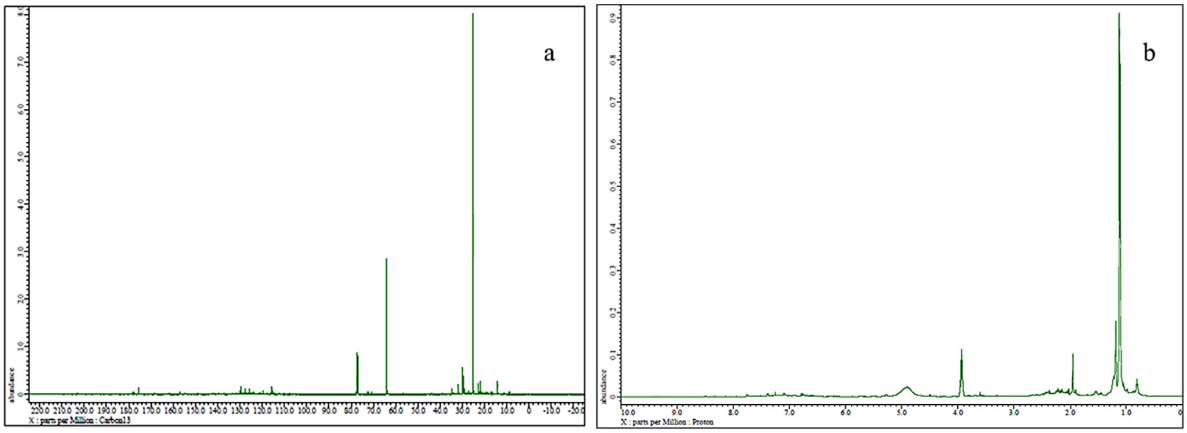


Fig. 2. ^{13}C NMR (a) and ^{1}H NMR (b) spectra of tar derived from pyrolysis of MSW and coal mixture at 800 °C.

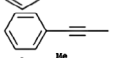
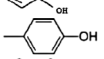
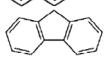
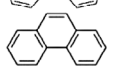
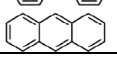
can also contribute to a better perception of the chemical structure of the mixture (MSW and coal). Moreover, Mao et al. [15] reported that the advanced NMR technique is able to detect small alterations on a molecular level by documenting the loss of volatiles and the formation of oxygenated groups. Besides, Rongbao and Bailing [16] alleged that the main property of NMR is its ability to associate resonances (ppm) in specific chemical shift ranges with specific structural features. Nevertheless, H and C groups associated with the ^{1}H and ^{13}C NMR spectra can yield structural information which helps to classify complex mixtures containing of aromatic, paraffinic, naphthenic and other compounds [17], it is also significant to study the cutoff points for selected sample concentrations in future research investigations. The total ion chromatograms of pyrolytic tar from the mixture of MSW and coal were analyzed, and 20 major compounds were identified which are shown in Table 2. The majority of compounds were aromatics (benzene, ethylbenzene, toluene, xylene and others). Provided a reaction partner is available and the temperature is increasing to higher temperatures of 800–850 °C, mainly tertiary tars, such as naphthalene and polyaromatic hydrocarbons (PAHs), were formed. Hence, the major compounds of aromatics in pyrolytic tar were a logical consequence. The same conclusions were drawn by Zhang et al. [18], who pyrolyzed a wet sewage sludge and claimed that the high temperature could reduce the tar yields and had significant influence on its composition, such as PAHs (naphthalene, benzene, toluene, xylene), generated rapidly when the temperature increased above 700 °C. Perng [19] obtained similar results by heating a poly(ether imide) sample step by step and reaching 800 °C, which enhanced the partial decomposition and pyrolysis/gasification of some macromolecules, causing the formation of smaller molecules [20].

It is noteworthy that there were a number of oxygenated compounds with reactive molecules which belong to the decomposition of hemicellulose and cellulose [21]. Likewise, phenols and cresols are phenolic compounds produced from lignin [22,23]. In this study, phenolic compounds such as phenol, 2-methyl- and p-cresol were also detected in the pyrolytic tar composition of the mixture MSW and coal.

4. Conclusion

The characterization of pyrolytic tar derived from the mixture of MSW and coal pyrolysis at the temperature of 800 °C was investigated using NMR and GC–MS. The results of the NMR analysis indicate that MSW plays a significant role on the composition and proportion of H and C bonds. Moreover, the results show that advanced NMR spectroscopic techniques applied in this study can also contribute to a better understanding of the chemical structure of the mixture (MSW and coal). The results of GC–MS analysis of the pyrolytic tar indicate that tar contains 20 major components and almost all of these components are aromatics due to the pyrolysis temperature. This is logical, since the pyrolysis process was conducted at the temperature of 800 °C (high-temperature carbonization) which will produce a substance that contains more of the aromatics. Hence, the findings of this study lead to conclusions on the aromaticity of the produced tar. Further investigation will be carried out at lower temperature conditions to investigate the effect of temperature as well as individual samples of coal and MSW fractions.

Table 2. Major compounds in pyrolytic tar from the MSW and coal mixture.

Peak. No	Retention time ,min	Compound	Mol. Weight, g/mol	Formula	Structure	Group*
1	2.45-2.47	Benzene	78.114	C_6H_6		AR
2	3.84-3.85	Methyl Isobutyl Ketone	100.16	$C_6H_{12}O$		KT
3	4.47-4.48	Toluene	92.141	C_7H_8		AR
4	7.1	Boric acid	61.831	H_3BO_3		AC
5	7.49-7.50	Ethylbenzene	106.168	C_8H_{10}		AR
6	7.82	P-Xylene	106.1650	C_8H_{10}		AR
7	7.82	o-Xylene	106.1650	C_8H_{10}		AR
8	8.63	Styrene	104.15	C_8H_8		AR
9	11.91	Phenol	94.113	C_6H_6O		AR
10	13.93-13.94	Benzene, 1-propynyl-	116.1598	C_9H_8		AR
11	14.34	Phenol, 2-methyl-	108.1378	C_7H_8O		PH
12	15.07	P-Cresol	108.13	C_7H_8O		PH
13	18.47	Naphthalene	128.1705	$C_{10}H_8$		AR
14	20.14	Quinoline	129.16	C_9H_7N		AR
15	21.67-21.68	Naphthalene, 1-methyl-	142.201	$C_{11}H_{10}$		D-AR
17	25.84	Acenaphthylene	152.196	$C_{12}H_8$		AR
18	29.12	Fluorene	166.223	$C_{13}H_{10}$		AR
19	33.62	Phenanthrene	178.234	$C_{14}H_{10}$		AR
20	33.62	Anthracene	178.234	$C_{14}H_{10}$		AR

AR-aromatic, AC-acidic, PH-phenolic, KT-ketone, D-AR-di-aromatic

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